

# ISOTOPIC FRACTIONATION MECHANISM: A KEY TO INTERPRETATING ISOTOPIC COMPOSITION OF CALCITE AT AQUIFER OUTLET AS HYDROSYSTEM DYNAMIC

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**Abstract:** The isotopic composition of the calcite that precipitates at the level of springs outlets records the hydrodynamic variations of the hydrosystems. However, to be able to decipher this recording, it is necessary to understand the kinetic isotopic fractionations. A mathematical approach has been developed to reproduce the chemical and isotopic partition during calcite precipitation and CO<sub>2</sub> degassing. The approach correctly reproduces the evolutions observed *in situ*. The following step remains the integration of environmental parameters to field constraints on the model (flow, water level...).

## 1. INTRODUCTION

Groundwater is an essential water resource. However, the availability of this water resource depends both on the evolution of climatic conditions and on human activities that impact aquifer recharge as well as water quantity and quality. In the context of global changes, a good understanding of the behavior of aquifer systems, particularly the conditions of their sustainability, is essential to better manage these water resources.

At the level of carbonate aquifer springs, the calcite that precipitates records the evolution of the hydrosystems. Indeed, the quantities of precipitated calcite, their location in relation to the spring, and their chemical and isotopic composition (<sup>18</sup>O and <sup>13</sup>C) are directly dependent on (i) the flow rate of the spring, (ii) the conditions of recharge of the aquifer, and (iii) the meteorology. The "reading" of the records contained in such calcites could therefore be used to understand the impact of global changes on the behavior of these hydrosystems [1].

However, the isotopic fractionations associated with calcite precipitation are not representative of an equilibrium, but rather a kinetic partition where isotopic disequilibrium remain poorly understood [2-4]. Understanding such kinetics systems is therefore essential to use the potential of these carbonates.

## 2. METHODS

During 2 years, L. Fleurent (2015) [4] monitored geochemical parameters (water chemistry,  $\delta^{13}\text{C}_{\text{TDIC}}^1$ ,  $\delta^{13}\text{C}_{\text{calcite}}$ ) of the Ours Spring, a carbo-gaseous spring located in the Massif Central (France). A mathematical approach has been developed to reproduce the evolutions observed *in situ*. It is based on both chemical and isotopic reactions, where CO<sub>2</sub> degassing, calcite precipitation and isotopic fractionation during phase changes are taken into account. Three parameters (one for the

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<sup>1</sup> TDIC, Total Dissolved Inorganic Carbon

degassing part and two others for the calcite precipitation part) as well as the isotopic fractionation factors are used to fit the simulated isotopic and chemical data on the measured values.

### 3. RESULTS

The mathematical approach correctly reproduces the  $\delta^{13}\text{C}$  evolution of the TDIC against that of the water chemistry (Figure 1a). To optimize the calibration, the isotopic fractionation factors used in the calculations do not correspond to the equilibrium values of the literature. For calcite, the evolution of the  $\delta^{13}\text{C}$  values is less well reproduced in particular for two points (Figure 1b). In such a case, the difficulty of calibration may be related to the sample characteristics: the calcite analyzed accumulated during several days, while the water chemistry and the carbon  $\delta^{13}\text{C}_{\text{TDIC}}$  are discrete measurements.

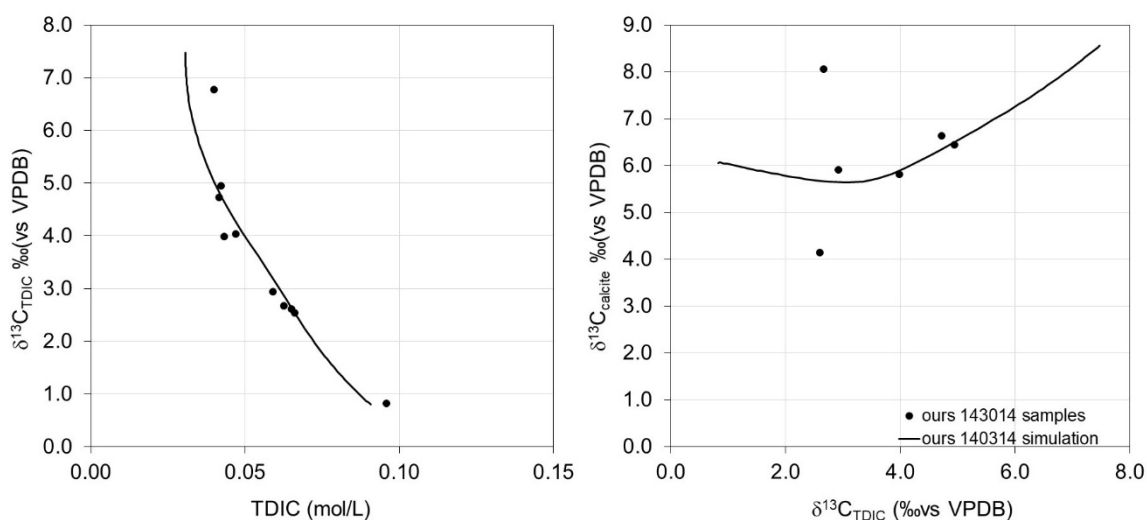


Figure 1.  $\delta^{13}\text{C}$  evolution of the total dissolved inorganic carbon with total dissolved inorganic carbon concentration (TDIC) and  $\delta^{13}\text{C}$  evolution of calcite with  $\delta^{13}\text{C}$  of total dissolved inorganic carbon.

### 4. CONCLUSIONS

The coupled approach gives good results for the liquid fraction and still needs to be tested for the precipitated fraction. The next step of this research project will consist to relate the values of calibration parameters and the isotopic fractionation factors to concrete variables such as the flow rate of the spring and the thickness of the water, an objective that will requires acquiring of new data.

### REFERENCES

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